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Room-temperature chemical vapor deposition and mass detection on a heated atomic force microscope cantilever

Erik O. Sunden, Tanya L. Wright, Jungchul Lee, William P. King,[a] and Samuel Graham[b]
Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0405

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This letter reports the localized room-temperature chemical vapor deposition of carbon nanotubes (CNTs) onto an atomic force microscope cantilever having an integrated heater, using the cantilever self-heating to provide temperatures required for CNT growth. Precise temperature calibration of the cantilever was possible and the CNTs were synthesized at a cantilever heater temperature of 800 °C in reactive gases at room temperature. Scanning electron microscopy confirmed the CNTs were vertically aligned and highly localized to only the heater area of the cantilever. The cantilever mechanical resonance decreased from 119.10 kHz to 118.23 kHz upon CNT growth, and then returned to 119.09 kHz following cantilever cleaning, indicating a CNT mass of 1.4×10^{-14} kg. This technique for highly local growth and measurement of deposited CNTs creates new opportunities for interfacing nanomaterials with microstructures. © *2006 American Institute of Physics*.
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The unique properties of nanostructured materials have generated widespread interest and motivated advancements in their synthesis and characterization. While nanomaterials properties are by no means fully understood, there is a lack of techniques to exploit their unique properties; in particular, there is a need to interface nanomaterials with microscale and macroscale platforms. The integration of nanomaterials with microelectronics, microelectromechanical systems (MEMS), and macroscale sensors has been previously demonstrated with directed self-assembly,[1] directed growth on micropatterned catalytic sites,[2] spin casting,[3] and electrophoretic trapping.[4] While these integration techniques are scalable, they require global exposure of the device to the processing procedure, which may risk contamination and/or make the process incompatible with complementary metal oxide semiconductor processing. Local synthesis can circumvent these risks, facilitating nanomaterial integration in only desired areas while leaving the remainder of the device platform unaffected.

Carbon nanotubes (CNTs) are perhaps the most widely investigated nanomaterial because of their thermal,[5] electrical,[6] and mechanical[7,8] properties. The chemical vapor deposition synthesis of CNTs typically requires temperatures to 900 °C and processing windows greater than 100 min, most of which is attributed to the heating and cooling of the synthesis chamber. This high temperature renders impossible direct CNT synthesis on most MEMS and electronics. CNT growth in a room-temperature reactive gas onto microfabricated heaters is significantly faster than CNT growth in a furnace because of the extremely small thermal mass of the microheater, and further offers highly local control of CNT growth.[9] While the localized synthesis of carbon nanostructures onto a microfabricated heater has been demonstrated,[9] this work did not employ local temperature calibration, nor was it capable of integrated quantitative assessment of the CNTs.

This letter reports a novel method for selectively synthesizing CNTs directly onto the tip of a heated atomic force microscope (AFM) cantilever via chemical vapor deposition (CVD), using only the heating of the probe. Like previous research into CNT growth onto micro-heaters, this approach eliminates the need for chemical processing and ambient CVD temperatures that might otherwise damage sensitive microfabricated features. The present letter additionally demonstrates integration of functional nanostructures into a microscale sensing device that allows *in situ* characterization of the CNTs.

The experiment used a heatable atomic force microscope cantilever fabricated by our group at Georgia Tech following a documented process.[10] Similar cantilevers were designed for data storage[11] and have since been shown to be capable of highly sensitive metrology[12] and nanomanufacturing.[13] Electron beam evaporation deposited 10 nm iron catalyst film onto the cantilever prior to temperature calibration. The electron beam evaporated film was sufficiently thin to form islands upon heating;[14,15] each island acts as an individual growth site for CNTs.

Laser Raman thermometry calibrated the temperature of the heated AFM cantilever to within 4 °C.[16] Resistance versus voltage data were collected before and after the iron catalyst deposition and during the Raman temperature measurements. Inspection of these data ensured that the electrical functionality of the device remained constant. The cantilever temperature calibration was performed using a Raman spectrometer operating in 180° backscattering geometry. The cantilever heater was excited by a 488 nm Ar^+ laser and the scattered light was collected by a 0.25 m focal length spectrometer with a 3000 l/mm grating. The laser power at the sample was 57.3 μW and the collection time was 60 s. For these conditions, the laser did not produce heating in the cantilever. The Stokes shift was linear with temperature between 300 and 1300 K, resulting in a simple device temperature calibration. The measured temperature was linear with input power to the device and thus a desired surface temperature could be obtained by controlling the input power. Ra-

[a]Electronic mail: William.King@me.gatech.edu
[b]Electronic mail: Samuel.Graham@me.gatech.edu

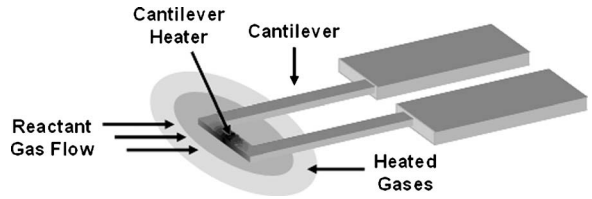

FIG. 1. The heated atomic force microscope cantilever is suspended in room-temperature reactant gases. An internal resistive heater in the cantilever heats the gases flowing over the cantilever, such that chemical vapor deposition occurs only on the heater.

man measurements confirmed the presence of localized heating at the free end of the AFM cantilever in the small resistive low-doped region. Additional details of the temperature profile have been published elsewhere.[16]

Following the electrical and temperature calibrations, the cantilever was mounted into a 2 in. quartz tube, with electrical connections from the cantilever to external driving electronics. Figure 1 shows the experimental setup. Argon purged the tube for 2 min prior to the introduction of the hydrocarbon reaction gases and the cantilever heating. Following the purge, methane, hydrogen, and acetylene were introduced and controlled by individual mass flow controllers at flow rates of 1000, 500, and 100 sccm, respectively, for the duration of the growth period. During the trial, the cantilever was heated to 800 °C for 15 min. To achieve synthesis onto the cantilever heater region, the near-field temperature surrounding the heater region must be great enough to induce decomposition of the carbonaceous gases. At the end of the soak period, the cantilever was powered down and argon was reintroduced to purge the remaining hydrocarbons. The entire process was performed at atmospheric pressure and without background furnace heating.

Figure 2 shows scanning electron microscopy (SEM) images of the cantilever after processing, having vertically aligned CNTs covering the cantilever heater region. The CNTs were approximately 5–10 μm in height and of diameter in the range of 10–30 nm. Although the entire cantilever was coated in catalyst, the growth of CNTs was limited solely to the heater region, demonstrating the selectivity possible via this method. Raman microscopy determined that the CNTs were highly graphitic with a graphitic to defect band intensity ratio greater than 2. The vertical array of nanotubes displayed a slight Gaussian profile across the length of the heater region, providing possible clues to the temperature field in the cantilever and in the surrounding gas. Based on our experiments with heated ambient environments, an ambient temperature greater than 700 °C is required to create the aligned CNT arrays from 10 nm thick iron films.

Microcantilevers are capable of highly sensitive detection of changes in mass adhering to the cantilever through changes in cantilever resonant frequency.[17] Our Asylum MFP-3D AFM system measured the resonance properties at each stage in the processing. Figure 3 summarizes these results. The cantilever resonant frequency decreased from 119.73 to 119.10 kHz, or about 0.52%, due to the iron deposition, and then again 119.10 to 118.23 kHz, or about 0.73%, due to CNT growth. To ensure that we were indeed detecting CNT mass, the cantilever was self-heated to 900 °C in air, a process that reliably oxidizes and removes CNTs. SEM verified that the cantilever was cleaned in this cleaning step. Following cleaning, the cantilever resonant frequency increased to the pre-CNT value of 119.09 kHz. The change in mass due to CNT growth (Δm) can be modeled as $\Delta m = k(f_2^{-2} - f_1^{-2})/4\pi^2$, where k is the cantilever spring constant and f is the cantilever resonant frequency.[17] Typically this equation has a constant coefficient multiplier to account for the distribution of mass along the length of the cantilever, but in this case all of the CNTs are located at the cantilever free end and no multiplier is required. The cantilever spring constant was 0.536 N/m and thus we estimate that the mass of grown CNTs is close to 1.4×10^{-14} kg. This mass is consistent with estimates of the nanotube volumetric coverage ob-

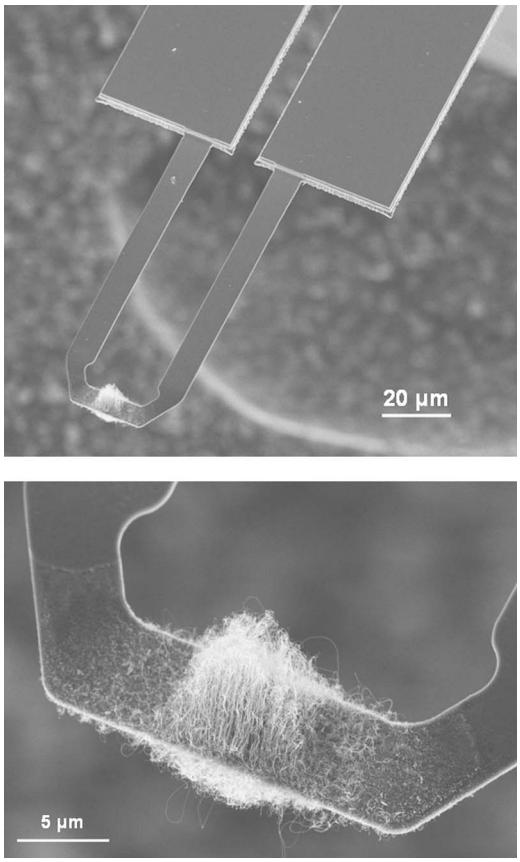

FIG. 2. Carbon nanotubes grow only on the heated region of the cantilever.

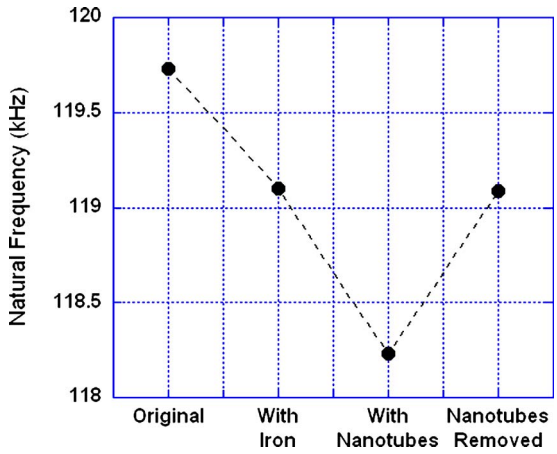

FIG. 3. Cantilever resonance measurements before and after iron deposition, after carbon nanotube growth, and after cantilever cleaning. The cantilever resonance shifted, as would be expected for mass increase in the first two processes steps and returned to its prenanotube value after cleaning. The mass of nanotubes grown on the cantilever was estimated at 4×10^{-14} kg.

served in SEM and assuming a density of graphite of 1.7 g/cm^3. The cantilever was further characterized with periodic heating with the goal of thermogravimetric measurement of the CNT mass, but we were unable to produce definitive results. Finally, the cantilever was characterized with force-distance curves.[18] The nanotubes exhibited a spring constant of 10^2 less than the cantilever.

Much work has been reported on the use of CNT tips for AFM for which there are several manufacturing methods including arc discharge,[19] thermal chemical vapor deposition,[20] and hot filament CVD,[21] and in fact CNT-tipped cantilevers are commercially available.[22] The fabrication of the heated AFM cantilever is much more complex than fabrication of a common silicon or silicon nitride cantilever, and the approach described here will probably not replace these other, simpler techniques. However, the present technique could integrate any CVD-synthesized material onto a highly functional microsensor and could improve sensors based on microheaters.[23] The approach could be performed with other types of AFM cantilevers having integrated heaters. For example, piezoresistive AFM cantilevers can be heated if operated at high power,[23] but in general piezoresistive cantilevers are not well suited to high-temperature operation and do not have resistive elements at the free end. The present synthesis was performed at 800 °C, and in general at least 700 °C is required to produce CNTs,[24] although other nanomaterials could be synthesized at lower temperature.

This letter reports the room-temperature synthesis of CNTs onto heated AFM cantilevers and resonance-based mass detection using the same cantilevers. Cantilever resonance experiments indicate the CNTs were 1.4×10^{-14} kg. This technique for highly local materials growth and measurement is compatible with any CVD material, and creates novel opportunities for interfacing nanomaterials with microstructures.

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